Electrochemical investigation on the carbonate and phthalate-plasticized polyacrylonitrile based polymer electrolytes

W.G. Chong and Z. Osman*

Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author: zurinaosman@um.edu.my

*Tel: +603-79675932
*Fax: +603-79576478

Abstract

Polymer electrolytes consist of polyacrylonitrile (PAN), lithium tetrafluoroborate ($LiBF_4$), ethylene carbonate (EC) and dimethyl phthalate (DMP) are prepared using solution casting method. The optimized composition gives high conductivity value of 1.08×10^{-2} S cm^{-1} at room temperature. The electrochemical properties of PAN-EC-DMP-$LiBF_4$ polymer electrolytes and the discharge characteristics of a Li/$LiCoO_2$ are investigated. The electrolytes show high electrochemical stability up to 4.4 V (versus Li^+/Li).

Keywords: Polyacrylonitrile; Lithium-ion battery; Impedance; Transference number; Voltammetry

1. Introduction

Lithium ion battery technology offers the highest energy density among the rechargeable battery technologies has dominated the market for mobile electronic devices for decades. The key to the success of development of novel and advanced rechargeable batteries are the materials. The components of the batteries have been extensively prepared and studied to improve the discharge capacity, safety and cycle life of the batteries.

Solid polymer electrolytes have received much attention due to its mechanical, electrochemical properties and structural integrity required for battery applications [1-5]. There has been extensive research on the physical and electrochemical properties of polymer electrolytes but the factors that contribute to the capacity loss are rarely studied. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) makes possible the elucidation of the kinetics of electrochemical reactions taking place at electrode surfaces [6, 7]. These methods afford an opportunity to provide primitive electrochemical redox reactions in solid polymer electrolytes with the electrodes.

A few attempts in the past to predict lithium-ion battery capacity have been reported. A 'first-principles' electrochemical model was used by Fuller et al. [8] to estimate lithium-polymer cell capacity. Spotnitz [9] incorporated solid-electrolytes interface (SEI) growth into Fuller's model and began to look into the correlation of impedance change with capacity fade.

This paper reports the preparation of PAN based polymer electrolyte plasticized with EC and DMP containing varied amount of $LiBF_4$. The electrochemical properties of polymer electrolyte were characterized using LSV and CV. Charge-discharge studies were also done on the Li/P30/$LiCoO_2$ cell at room temperature.

2. Experimental Methods

2.1 Sample Preparation

Polyacrylonitrile (PAN) with average molecular weight of 150,000 and lithium tetrafluoroborate $LiBF_4$ (98% purity) were obtained from Aldrich. The plasticizers ethylene carbonate (EC) and dimethyl phthalate (DMP) were supplied from Sigma-Aldrich and Merck, respectively. The solvent dimethylformamide (DMF) was obtained from R & M chemicals. All materials were used as received. PAN was dissolved in DMF at 60 °C. The plasticizers EC and DMP in the ratio of 1:1 were added into the PAN solution. Varied amounts of $LiBF_4$ (10-40 wt.%) were then added to the homogeneous solution and further stirring took place for several hours. The solvent was removed at 60 °C and 0.2 bar for 48 h.

2.2 Characterizations

The ionic conductivity of the polymer electrolytes was determined using electrochemical impedance spectroscopy (EIS) from room temperature to 353 K. The samples were sandwiched between stainless steel blocking electrodes. The impedance measurements were carried out using HIOKI 3532-50 LCR Hi Tester in a frequency range between 50 Hz and 1 MHz. The conductivity, σ of the SPE was calculated using the following equation:

$$\sigma = {}^{t}/_{R_b A} \quad (1)$$

where t is the thickness of sample, A is the contact area between electrode and sample in and R_b is the bulk resistance. The cationic transference number in the SPE was evaluated by the method that proposed by Evans et al. [21]. A fixed d.c. voltage, ΔV= 0.5 V is supplied to electrochemical cell in the configuration Li/SPE/Li until a steady state achieved, consequently initial (I_o) and final (I_s) currents are recorded. The cell is also subjected to a.c. impedance measurements prior to and after the polarization to evaluate the resistance before (R_o) and after (R_s) the polarization. The cationic transport number, t_+ can be estimated following equation:

$$t_+ = {}^{I_s(\Delta V - I_o R_o)}/_{I_o(\Delta V - I_s R_s)} \quad (2)$$

Voltammetric methods were used to determine the electrochemical window of the polymer electrolyte films. Linear sweep voltammetry (LSV) was performed on stainless steel working electrode, with counter and reference electrode of lithium metal at scanning rate of 1.0 mV/s using WonATech system. Cyclic voltammograms were recorded using a potentiostat/galvanostat at room temperature. In this method, a Li/ SPE/ Li cell was assembled by sandwiching the respective electrodes and the most electrochemically stable SPE film (predetermined from LSV) in a sealed container.

In order to examine the practicability of the PAN-based polymer electrolyte as electrolyte in a battery, the most electrochemically stable polymer electrolyte film which carries high conductivity at room temperature was used as the electrolyte for the lithium polymer cell fabrication. A Li/SPE/$LiCoO_2$ cell was assembled by sandwiching the respective electrodes and the SPE film in a sealed container. The size of the electrodes and electrolyte film was fixed at 4 cm^2. Charge/discharge cycling was carried out by using an electrochemical analyzer, WPG100e

potentiostat/galvanostat system with a constant current of 0.05 mA. The cycle test of the cell was performed in the 2.5-4.3 V range by a galvanostatic method. The charge-discharge process was repeated up to 20 cycles at room temperature. The cell was characterized by EIS before and after cycling. Data fitting was carried out with Zman software to acquire the equivalent circuit using the parameters obtained by fitting for each cycle.

3. Results and Discussion

The conductivity of the polymer electrolyte shows a linear relationship with the salt concentration. Fig. 1 shows the variation of conductivity of the system containing different amounts of $LiBF_4$ in weight percentage. On addition of $LiBF_4$ salt, the conductivity value shows a continuous increase until a maximum is achieved at 1.08×10^{-2} S cm^{-1} for film containing 40 wt. % of $LiBF_4$. The conductivity values of this system falls within the range as required for practical applications. The high conductivity of the SPEs may due to the presence of plasticizers. Plasticization aids ionic mobility by opening up the narrow rivulet of plasticizer rich phase. The increase in ionic conductivity with salt concentration is attributed to the increase in number of charge carrier. The presence of plasticizers provide effective dissociation of salt and creates the facile pathway for ionic conduction [10].

Fig. 2 shows the variation of current with time for the cell consists of polymer containing 30 wt.% of $LiBF_4$ subjected to d.c. When an electric field is applied to the polymer electrolyte, the cation constituent Li is carried toward the cathode by Li^+, $Li_2BF_4^+$, etc., while BF_4^-, $Li(BF_4)^{2-}$ etc. migrate toward the anode. Hence, the movement of both the cationic and anionic species contribute to the total ionic conductivity [11].

The difference between the fluxes of Li-containing species directed toward the cathode and anode was measured as the cationic transport number. After a certain time, a steady state is developed, where the current drop is due to the growth of passivation layers on the electrodes and the establishment of concentration gradient. The t_+ was calculated using equation (2) where the impedance and current before and after polarization can be obtained from the Cole-Cole plot and the current-time plot as shown in Fig. 2. The cationic transport number measurement was conducted on two highest conducing samples i.e. the sample containing 30 wt.% of $LiBF_4$ salt (P30) and 40 wt.% of $LiBF_4$ salt (P40). The t_+ for sample P30 and sample P40 was calculated as 0.16 and 0.17. The anionic species are apparently the main contributor to the total ionic conductivity. The t_+ values obtained in this present work are within the range from 0.1 to 0.3 for PAN-based polymer electrolytes and similar to that reported by Chloe et al. and Chen et al. [11, 12]. This behaviour illustrates the similarity in the conductivity mechanisms in the plasticized polymer electrolytes and conventional liquid electrolytes [13].

The electrochemical stability of the polymer electrolytes films were studied by linear sweep volttammetry (LSV) and cyclic voltammetry (CV) analysis. The current-voltage response curves of polymer electrolyte containing different concentrations of $LiBF_4$ are shown in Fig. 3 (a)-(d). The current onsets are detected between 3.5 - 4.4 V vs Li, which can be assigned to the decomposition voltages of the polymer

electrolytes. Kim et al. [14] has reported a PAN-EC-PC-$LiPF_6$ polymer electrolytes system which has a decomposition limit up to 4.3 V. In this work, the sample containing 30 wt.% of the $LiBF_4$ was found to be most electrochemically stable electrolyte film with anodic stability limit of ~ 4.4 V. In addition, the electrochemical stability test of the most electrochemically stable film polymer electrolyte , sample P30 was performed on symmetrical cell Li/P30/Li at room temperature by using cyclic voltammetry.

Fig. 4 presents the CV curves for 1^{st}, 5^{th} and 10^{th} cycle of cell Li/P30/Li. The broad nature of the redox peaks and the greater suppression of the magnitude of peak currents can be clearly observed even at fifth sweep in this system can be explained as the solvation effect of plasticizers. It was reported the addition of organic solvent to PAN based polymer electrolyte appears to influence the oxidation potential [15]. The accumulation of free plasticizers aggregates at the interface facilitates ions migration and causes the anodic current to increase faster in the following sweeps than that in the first anodic sweep and gives the CV feature (i) [16] . The redox peaks corresponding to anodic oxidation at 1.0 V and cathodic reduction at −1.0 V occur versus Li^+/Li. The peak currents tend to decrease markedly during the initial cycles may due to formation of passivation layer on electrode and stabilize afterwards. On cycling, there is no substantial change in the redox peak voltages and the overlapping of the subsequent sweeps indicates that the charge transfer reaction at the interface between the film and lithium metal is reversible and the polymer electrolyte is able to support fully reversible redox process. Thus, it can be concluded that sample P30 has sufficient electrochemical stability and provide better cycle stability for the operation in lithium battery system.

Fig. 5 represents the variation of voltage with the discharge capacity for selected cycles of the Li/P30/$LiCoO_2$ cell at room temperature. As fabricated, the cell with the optimized SPE exhibited an open circuit voltage of 3.8V. The highest capacity of 0.6 mAh achieved at the first cycle. This value is comparable to the discharge capacity of cell consists of poly(acrylonitrile-methylmethacrylate)-based microporous gel electrolyte reported by Zhang and coworkers [17]. However, the discharge capacity abruptly decreased after second cycle and approaching constant started from the fifth cycle. This result is consistent with the cyclic voltammogram displayed in Fig. 4. The initial irreversibility is due to the increase in interfacial impedance resulting from the precipitation of reduce species on the electrode surface or oxidation of the positive electrode, which is known to result in the formation of a necessary solid-electrolyte interface (SEI) [18].

4. Conclusions

The electrochemical properties of PAN-EC-DMP-$LiBF_4$ polymer electrolytes display stability up to 4.4 V that are sufficient to allow operation in a lithium battery. Cyclic voltammetry has provided preliminary information of the change in film resistance and the charge transfer kinetics within the cell.

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Figures

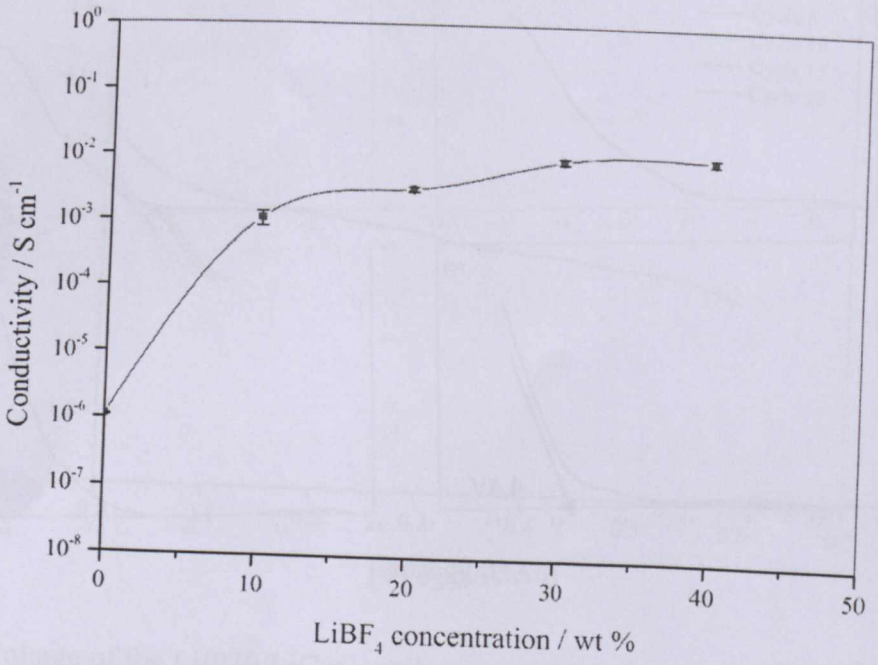

Fig. 1.Variation of conductivity with different amounts of $LiBF_4$

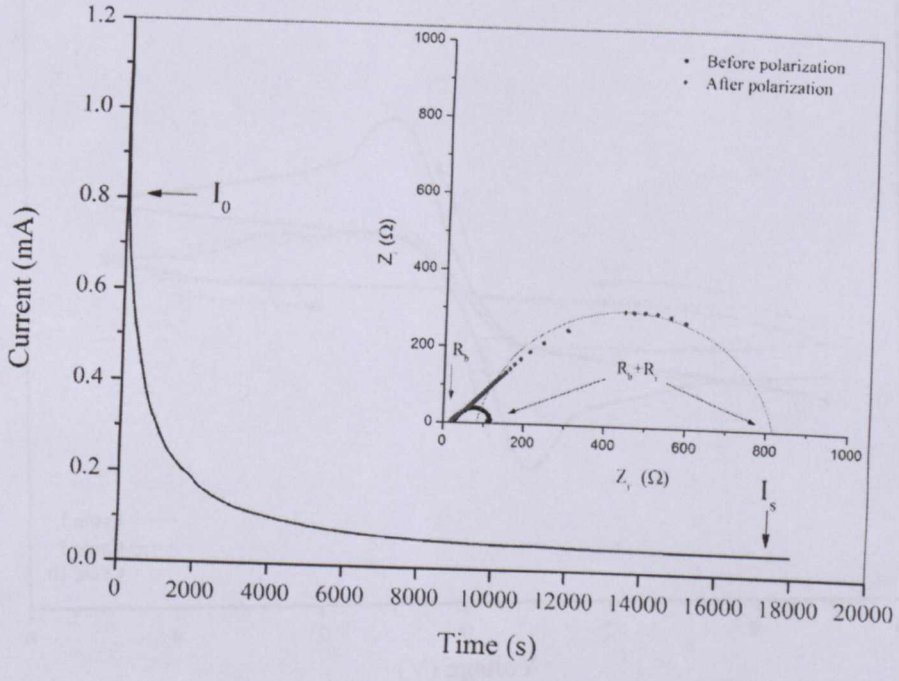

Fig. 2. Variation of current with time for the cell Li| P30 | Li subjected to d.c. polarization and the Cole-Cole plot of the of the cell before and after d.c. polarization (inset).

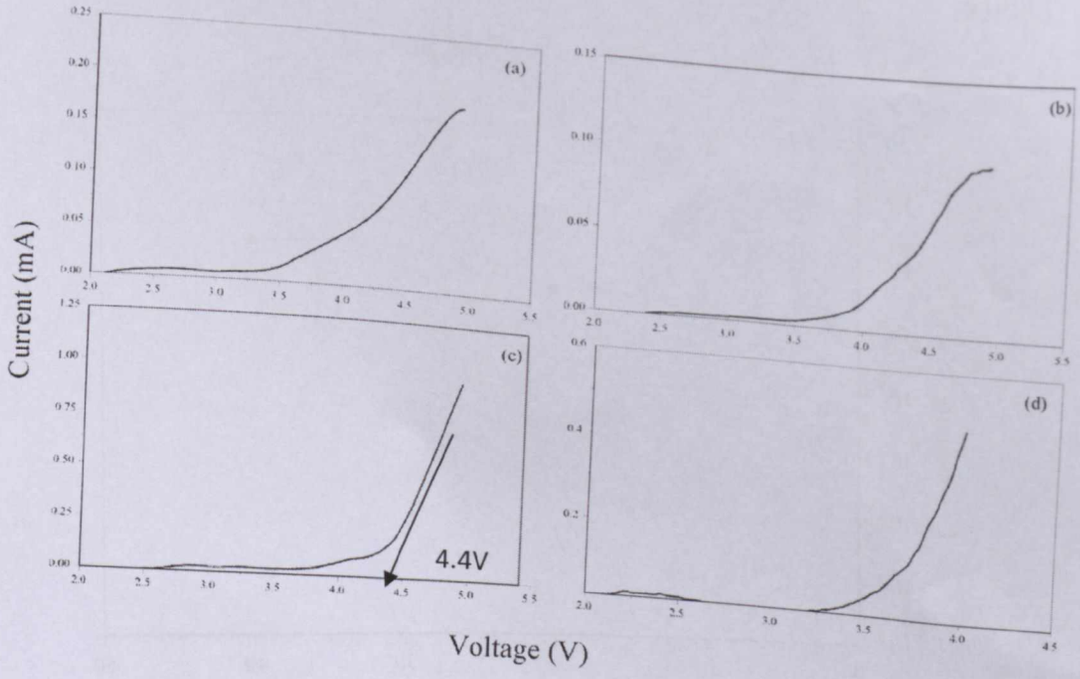

Fig. 3. Linear sweep voltammograms of the cell prepared with the PAN films containing (a) 10 wt.% (b) 20 wt.% (c) 30 wt.% (d) 40 wt.% of $LiBF_4$.

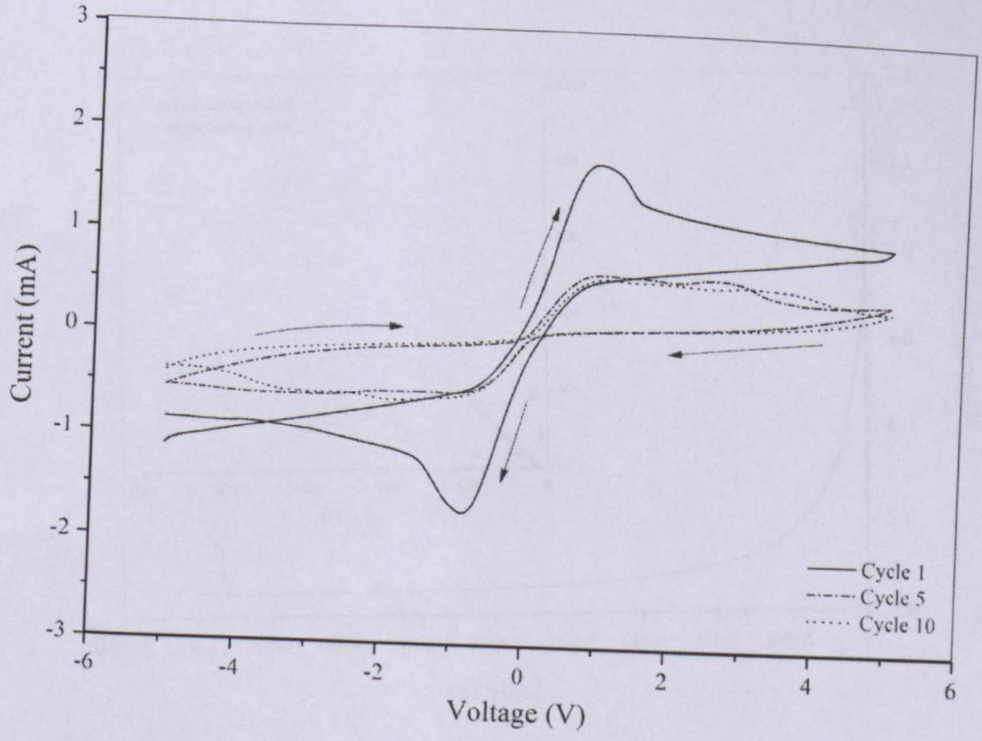

Fig. 4. Cyclic voltammogram of cell Li/P30/Li

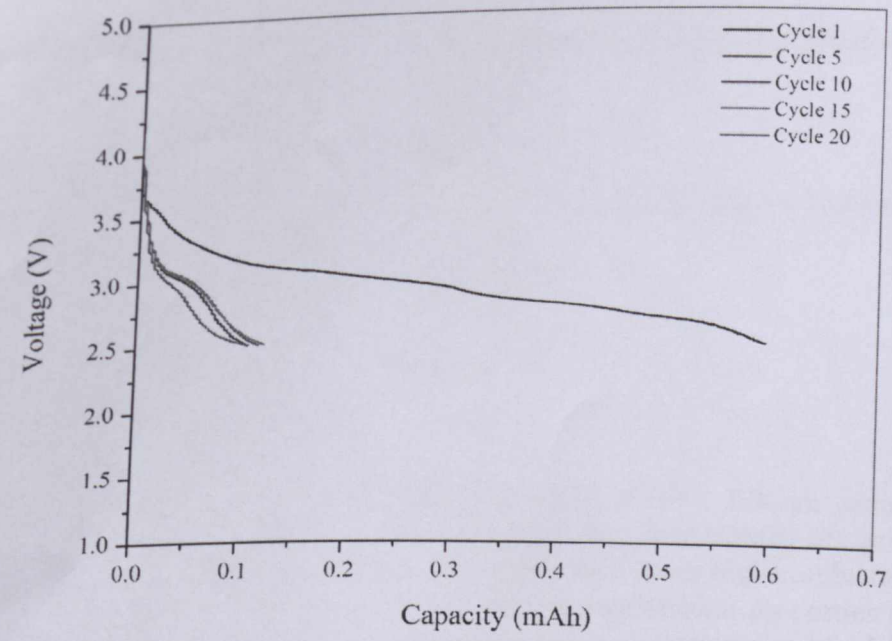

Fig. 5. Voltage of the Li/P30/$LiCoO_2$ cell versus capacity.